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THE EVAPORATION AND DEGRADATION OF N-NITROSO DIMETHYL
AMINE IN AQUEOUS SOLUTIONS

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Air Force Civil Engineering Center
Tyndall Air Force Base, Florida

March 1975

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THE EVAPORATION AND DEGRADATION OF N-NITROSO DIMETHYL AMINE IN AQUEOUS SOLUTIONS

ENVIRONMENTAL CHEMISTRY RESEARCH DIVISION
ENVIRONICS DIRECTORATE
AIR FORCE CIVIL ENGINEERING CENTER (OL-AA)
KIRTLAND AFB, NEW MEXICO

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greater in acid solution. Additional conclusions are that nitrite severely inhibits the photolysis of NDMA in acid and neutral pHs, and an increase in ionic strength slightly increases the evaporation rate. The implications of the above results for lagooning of the caustic NDMA waste streams are that the majority of the NDMA will volatilize from the solutions very rapidly unless the waste is neutralized. If the waste is neutralized, then photolysis would predominate unless nitrite is present, in which case, little of the NDMA would leave the lagoon either by volatilization or photolysis.



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PREFACE

This report was prepared by the Air Force Civil Engineering Center, Tyndall Air Force Base, Florida, under Job Order Number 21033W59. This report summarizes work done between February and March 1975. Captain Michael G. MacNaughton was project engineer and author, and Mr Thomas B. Stauffer was coauthor.

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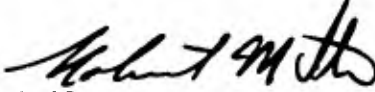
This report has been reviewed by the Information Officer (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


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TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION	1
II	EXPERIMENTAL	2
	1. Procedure	2
	2. Analytical	2
	3. Reagents	3
III	RESULTS	4
	1. Effects of pH	4
	2. Effects of Sunlight	4
	3. Effects of Photolysis	4
	4. Effects of Nitrite	4
IV	DISCUSSION	10
	1. Evaporation	10
	2. Photolysis	10
V	CONCLUSIONS	14
	References	15
	List of Symbols	16

LIST OF FIGURES

Figure	Title	Page
1	The Concentration of Aqueous NDMA as a Function of Time, pH, Ionic Strength, and Vessel Size	5
2	The Concentration of Aqueous NDMA as a Function of Time and pH in the Absence of Direct Sunlight	6
3	The Concentration of Aqueous NDMA as a Function of Time and pH in the Absence of Evaporation	7
4	The Concentration of Aqueous NDMA as a Function of Time and pH in the Presence of Nitrite	8
5	The Concentration of Aqueous NDMA as a Function of Time and pH in the Presence of Nitrite and in a Covered Vessel	9
6	The Concentration of Gas Phase NDMA as a Function of Time	13

SECTION I

INTRODUCTION

Knowledge of the mechanisms which control the transport and ultimate fate of pollutants in the environment is tremendously important in evaluating their environmental impact. The natural environment is an active reaction vessel where physical, chemical, and biological mechanisms act on the pollutant to either increase or decrease its environmental significance.

Nitrosamines have been of concern because of their reported carcinogenic effect on man. These compounds have been reported to be found in foods (Reference 1), soils (Reference 2), and sewage (Reference 3), and are an intermediate product in the manufacture of the rocket fuel unsymmetrical dimethyl hydrazine (UDMH). Because of the mutagenic properties of this organic compound, knowledge of the reactions which effect its transport and degradation in the natural environment is important if predictions are to be made on its environmental significance. The research reported here was designed to investigate the fate of N-Nitroso Dimethyl Amine (NDMA) in aqueous solutions and in a 25 percent caustic waste stream which is produced in the manufacture of UDMH.

References

1. N. Sen, et al, "Diethylnitrosamine and Other N-Nitrosamines in Foods," Analytical Chemistry, 52 (1969), p. 47.
2. A. Ayanaba, W. Verstraete, and M. Alexander, "Formation of Dimethylnitrosamine, A Carcinogen and Mutagen, in Soils Treated with Nitrogen Compounds," Soil Science Society of America, Proceedings, 37 (1973), p. 565.
3. A. Ayanaba, W. Verstraete, and M. Alexander, "Possible Microbial Contributions to Nitrosamine Formation in Sewage and Soil," National Cancer Institute Journal, 50 (1973), p. 811.

SECTION II

EXPERIMENTAL

These studies were designed to approximate varying environmental conditions which would effect the evaporation and/or degradation of NDMA in an open lagoon; however, no attempt was made to evaluate biological reactions which may occur over long residence times. Because of the number of variables which can influence evaporation and the goal of trying to produce results which can be used at other geographic locations, these studies were performed under occurring ambient conditions. Temperatures ranged from - 1 degree Centigrade to 21 degrees Centigrade, relative humidity from 8 to 100 percent and solar intensity from 0 to 76.7 langley's (grams-calories/centimeters²). The physical parameters given above were obtained from instruments at the location of the experiment and the Albuquerque National Weather Center.

1. PROCEDURE

Evaporation and photolysis experiments were conducted using 89-millimeter diameter pyrex petri dishes and a 39-millimeter diameter pyrex beaker which was cut off just above the 25 milliliter mark. For those experiments designed to measure photolysis in the absence of evaporation, the petri dish was covered with a pyrex plate onto which a capillary tube had been attached to allow sample withdrawal with a syringe needle.

Experiments were conducted in the following manner: 25 milliliters of the solution containing the NDMA was added to the pyrex petri dish, the container was weighed, and the sample was placed on a white surfaced table outside the laboratory. After the desired time interval, the sample was reweighed, the weight recorded, and the sample brought back to the original weight with all-glass distilled water. This allowed analysis of the sample without mathematically correcting for the concentration caused by water evaporation. After weighing, the samples were analyzed as described below and returned to the table outside the laboratory.

2. ANALYTICAL

Analyses were performed using a Tracor MT 222 gas chromatograph with a 6-foot by 1/4-inch stainless steel column packed with Porapak Q porous polymer beads. A Flame Ionization Detector was used with the following operating parameters:

Temperature: Oven - 217 degrees Centigrade
Inlet - 240 degrees Centigrade
Detector - 285 degrees Centigrade

Flowrate: Carrier - 70 milliliters/minute
Hydrogen - 43 milliliters/minute
Air - 470 milliliters/minute

NDMA gave a retention time of 4 minutes and a detection limit of 1 milligram/liter. Because of the low attenuation required (full scale sensitivity of 10×10^{-12} amps) and the resulting poor baseline, concentrations less than 5 milligrams/liter (25-nanogram per 5-microliter injection) were recorded as less than 5 milligrams/liter.

Samples from solutions containing NaOH were not injected directly but were first distilled using a conventional microorganic distillation apparatus. Twenty-five milliliters of distilled water were added to the sample and a distillate volume of slightly less than 25 milliliters was collected in an ice bath. The sample was brought up to 25 milliliters in a volumetric flask and analyzed as above. Recoveries of greater than 97 percent were achieved for 200-milligram/liter and 40-milligram/liter standards. Attempts at concentrating the samples by collecting the first 5 milliliters of distillate were unsuccessful since only 77 percent recovery could be achieved. However, if no water was added to the sample and the first 10 milliliters of distillate were collected, greater than 97 percent recovery could be achieved with a 2.5 fold concentration.

3. REAGENTS

All experiments were run using 99 percent pure reagent grade N-Nitroso Dimethyl Amine, Aldrich Chemical, supplied by the USAF Environmental Health Laboratory at Kelly Air Force Base, Texas. Because of the carcinogenic properties of this compound, it was kept in a sealed container and dilutions were made in a hood using a syringe. Concentrations were calculated from the weight difference observed in a volumetric flask. All other chemicals used in the study were analytical grade and the distilled water was initially deionized through a mixed media ion-exchange resin, distilled in an all-glass still and stored in a pyrex container.

SECTION III

RESULTS

1. EFFECTS OF pH

Figure 1 shows the reduction of NDMA as a function of time for neutral, acid, and caustic solutions. The reduction rate for caustic solutions is slightly higher for the neutral solutions which could be caused by the increased ionic strength. This is demonstrated by the 20 percent NaCl solutions which give a removal rate approximately the same as the caustic. Reducing the pH to 3.5 with 1 N HNO_3 produces a substantial increase in the rate of decrease.

2. EFFECTS OF SUNLIGHT

Figure 2 gives the plots of concentration versus time for neutral, acid, and caustic solutions located out of direct incident sunlight. Both H_2O_2 and H_2O_{2s} fall off at a lower rate; however, OH_s is not significantly different than OH.

3. EFFECTS OF PHOTOLYSIS

The degradation of NDMA in the absence of evaporation in the pyrex covered reaction vessel is shown in Figure 3. It is unclear why there is such a large amount of scatter in the data for the caustic solutions. It is apparent from the plot of the covered vessel located in the shade (H_2O_{ps}), Figure 4, that there is still some scattered UV which induces breakdown.

4. EFFECTS OF NITRITE

The plots of concentration versus time for neutral, acid, and caustic solutions in the presence of 5 percent sodium nitrite are given in Figure 4. Nitrite inhibits the removal in both the neutral and acid solutions but not in the 20 percent caustic. The effect of nitrite on photolysis is shown in Figure 5 where the concentration of NDMA versus time is shown for 5 percent nitrite solutions in pyrex covered vessels.

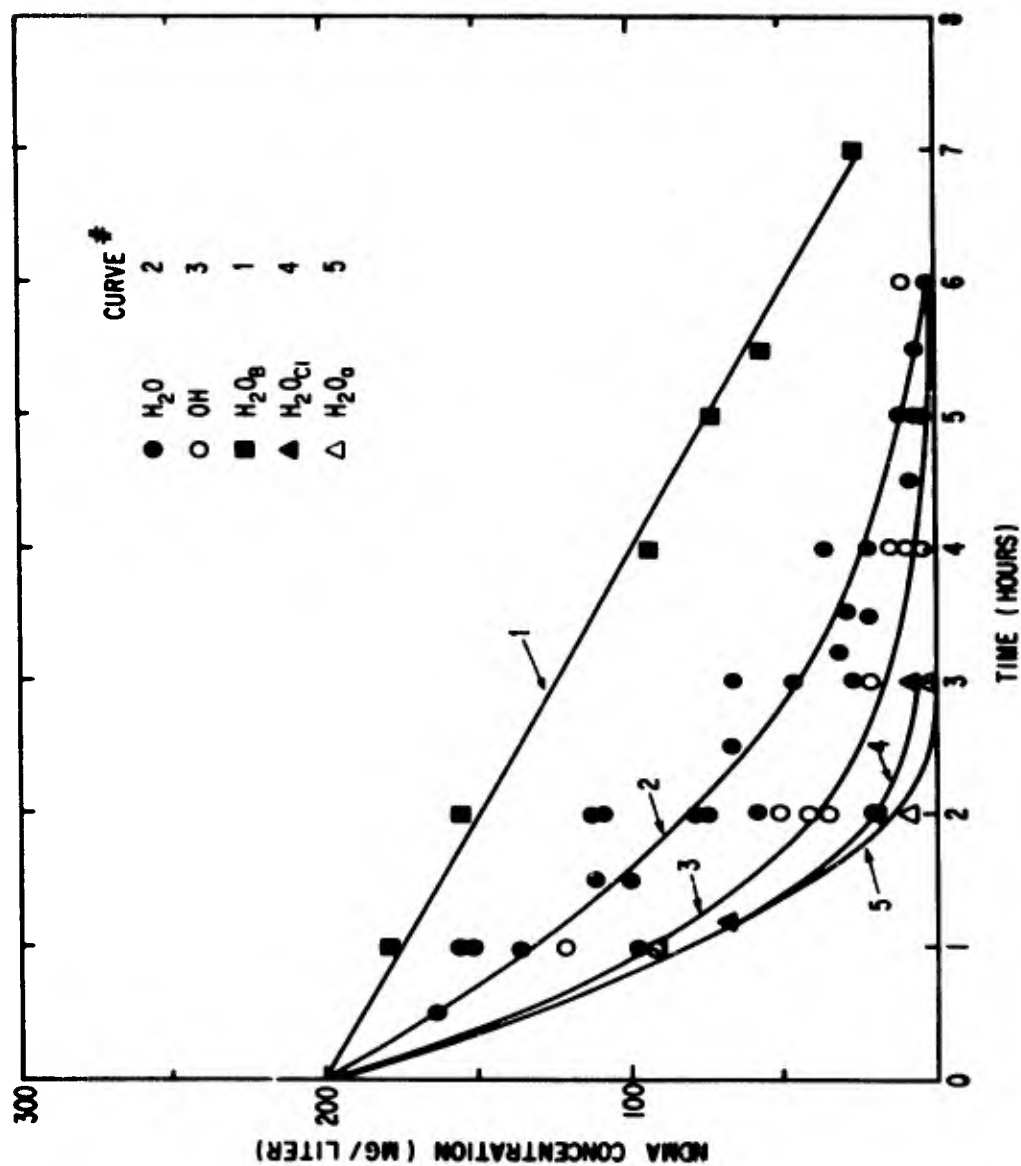


Figure 1. The Concentration of Aqueous NDMA as a Function of Time, pH, Ionic Strength, and Vessel Size

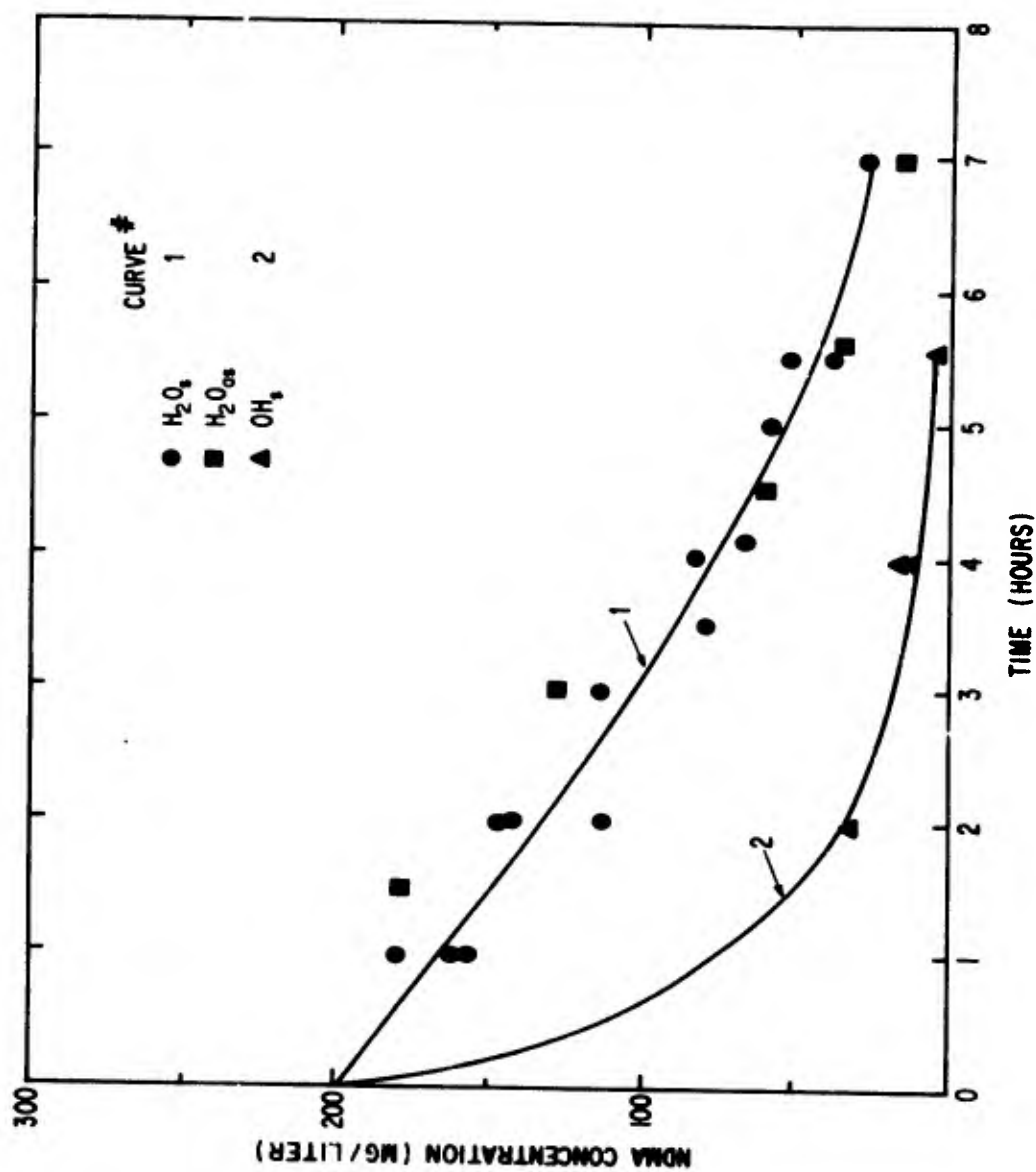


Figure 2. The Concentration of Aqueous NDMA as a Function of Time and pH in the Absence of Direct Sunlight

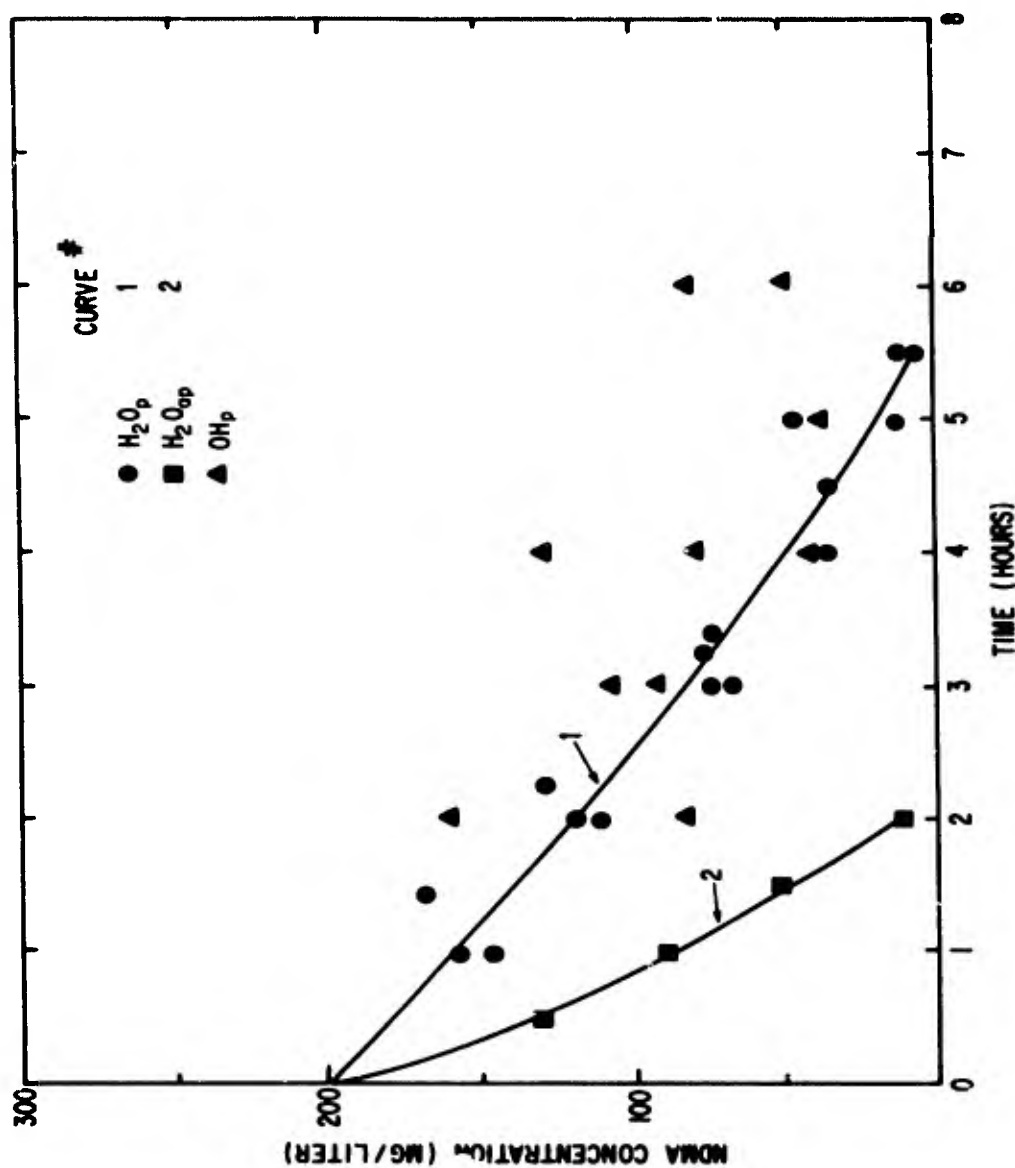


Figure 3. The Concentration of Aqueous NDMA as a Function of Time and pH in the Absence of Evaporation

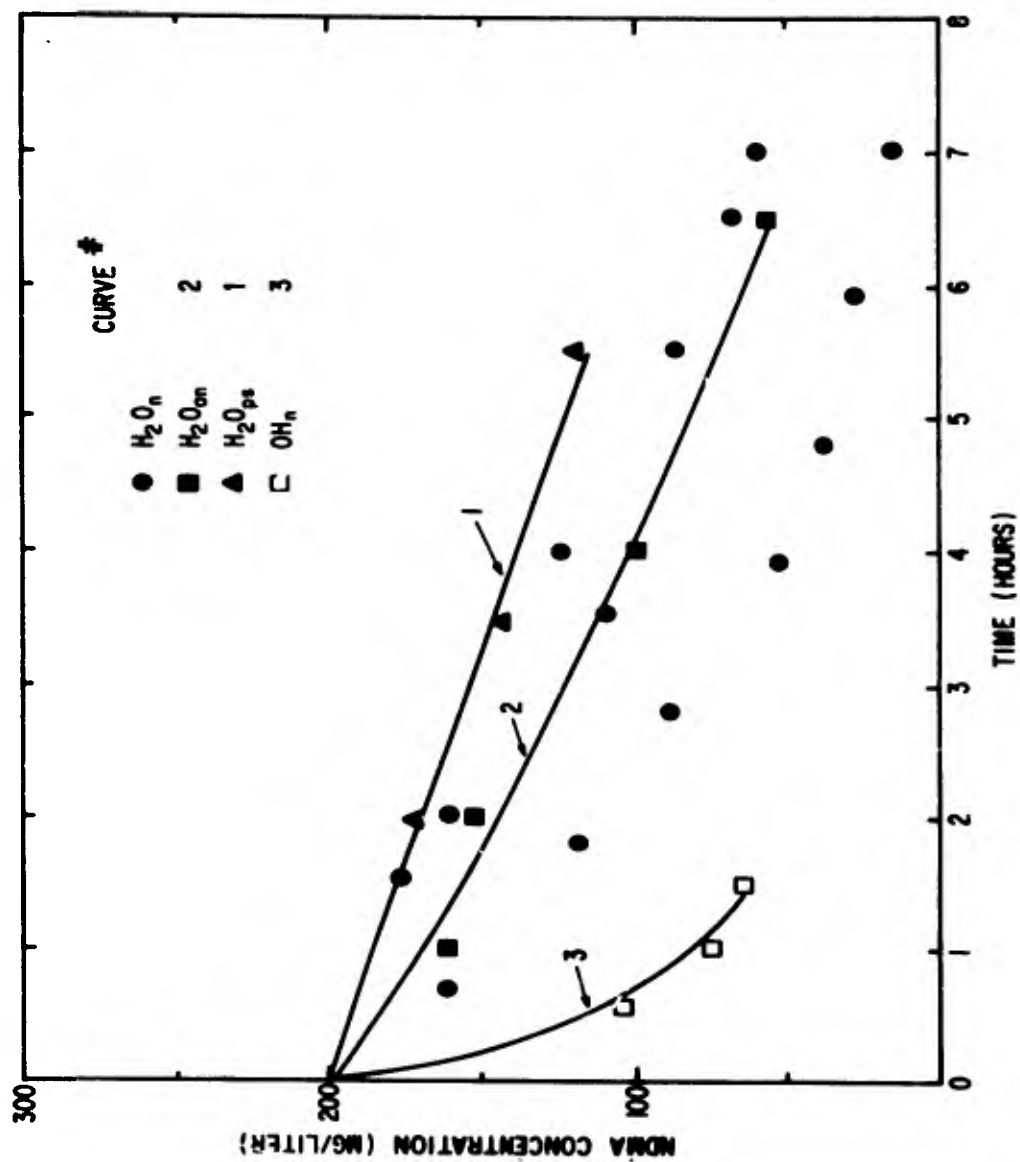


Figure 4. The Concentration of Aqueous NDMA as a Function of Time and pH in the Presence of Nitrite [A curve of a covered vessel in the shade is shown for comparison (H_2O_2ps).]

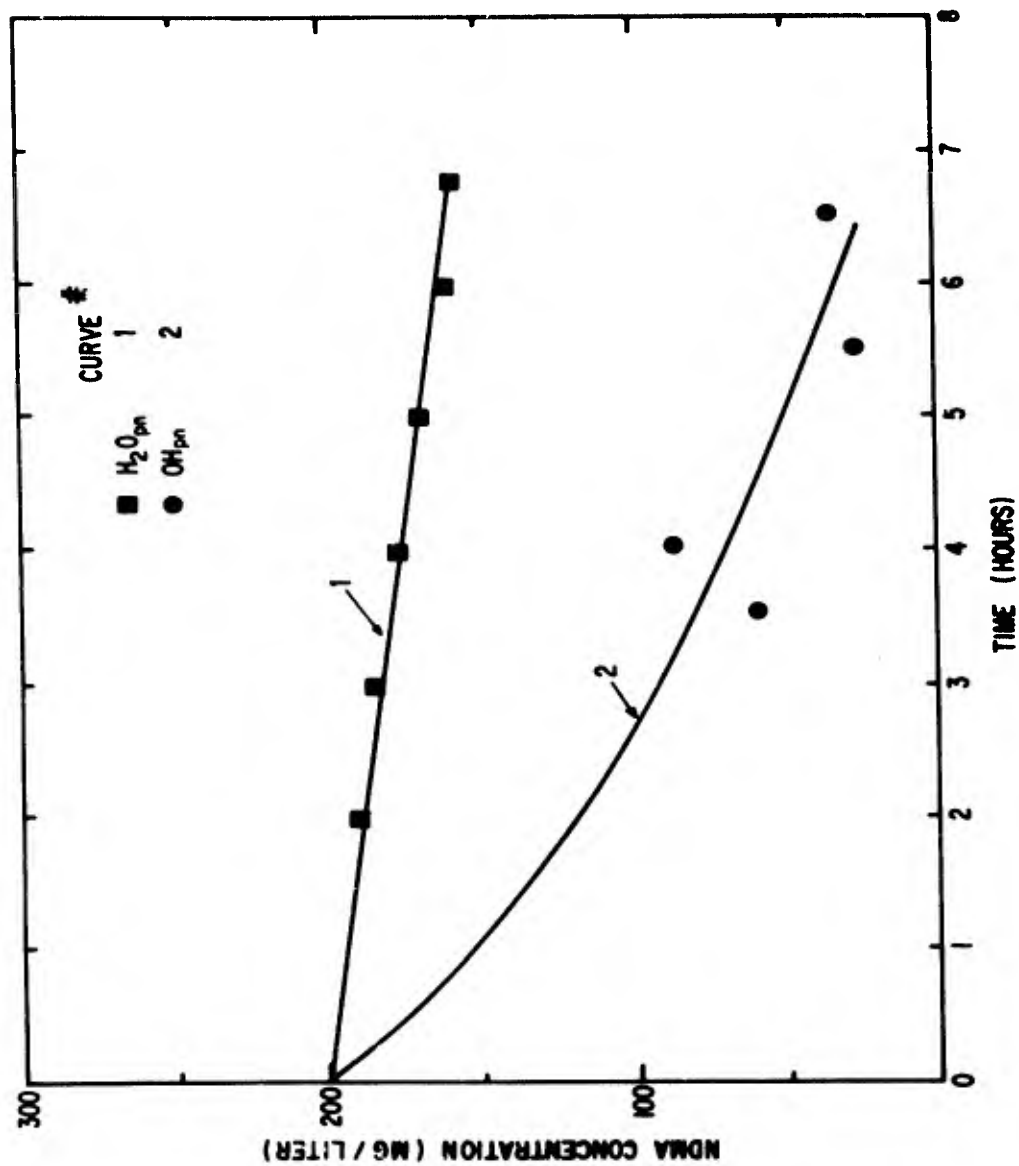


Figure 5. The Concentration of Aqueous NDMA as a Function of Time and pH in the Presence of Nitrite and in a Covered Vessel

SECTION IV

DISCUSSION

1. EVAPORATION

A review of the pertinent literature revealed no past research on the evaporation of NDMA. Figure 1 does indicate, however, that due to evaporation and photolysis, this organic compound disappears very rapidly from solution, with acid solutions giving a somewhat higher removal ($T_{1/2} \sim 0.8$ hour) than the caustic ($T_{1/2} \sim 0.9$ hour) or water ($T_{1/2} \sim 1.6$ hours).

For the same volume of solution, decreasing the available surface area (increasing the depth) caused a substantial change in the fall-off rate with the $T_{1/2}$ increasing to approximately 4 hours. Calculations on the reduction per unit surface area, however, gave higher removals for the deeper samples. This is probably due to the constant degradation caused by UV photolysis which is independent of depth in clear solutions of the moderate depth used here.

The significance of pH on evaporation (excluding the majority of the photolysis) can be seen by comparing the three curves in Figure 2 for those samples located out of the direct sunlight. For basic solutions, the removal is essentially the same as in the sun; indicating, evaporation is the predominate loss, whereas, for acid solutions, evaporation is low. In neutral solutions the evaporation accounts for about one half the removal.

Attempts to correlate water evaporation with NDMA gave poor results. However, as would be expected, the higher the evaporation rate of water the greater the rate of NDMA volatilization.

2. PHOTOLYSIS

There are several reports in the literature describing the photolytic decomposition of NDMA in the presence of acids. In one study, the nitrosamines were reported to be converted to amidoximes, secondary amines, alkyldenemines, and other compounds. The ultimate products of the photochemical reaction being aldehydes and ketones (Reference 4). The role of the acid in the photolysis is not clear; however, nitrosamines have been shown to form hydrogen bonded 1:1 complexes with an acid (Reference 5). The photo-

References

4. Yuan-Lang Chow, "Photolysis of N-Nitrosamines," Tetrahedron Letters, 34 (1964), p. 2333.
5. A. L. Fridman, F. M. Mukhametshin, and S. S. Novikov, "Advances in the Chemistry of Aliphatic N-Nitrosamines," Russian Chemical Reviews, 40 (1) (1974), p. 34.

lytic decomposition of NDMA is reported to be brought about by wavelengths in the UV diffuse absorption bands between 3200A and 3900A, as well as shorter wavelengths in the vicinity of the mercury line at 2537A. The shorter wavelengths also cause the decomposition of the resulting reaction products to N_2 , H_2 , CH_4 , C_2H_2 , and NO (Reference 6). No prior research has investigated the photolytic decomposition in basic solutions.

The degradation of NDMA by sunlight was investigated in a short study with a half life of 9.5 hours being measured. The resulting photolyzed solution showed no carcinogenic properties as compared to the non-photolyzed solutions (Reference 7).

It is apparent that the addition of nitrite greatly effects the photolysis at neutral and acid pH. This is understandable if nitrite is produced in the photolysis reaction. In a 5 percent nitrite solution, the removals are comparable to those found for samples located in the shade. Covering the vessels with pyrex to stop evaporation and limit the reduction to photolysis resulted in a decrease of only 40 milligrams/liter NDMA in 7 hours. This same effect of nitrite was not observed for caustic solutions. This implies that the chemical reaction is different at the high pH values. Since the photolysis encountered in the experiments reported here was brought about by sunlight and the cut off for incident solar radiation is above 2900A, the nitrite produced must come from the reaction of the radiation above this wavelength. Further evidence of nitrite production upon UV photolysis is given by the reported analytical procedure which uses this reaction and subsequent analysis of the nitrite to measure NDMA (Reference 8).

Analysis of the nitrite formed in samples placed in the sun during this investigation gave the following results:

<u>Sample</u>	<u>NDMA Lost (milligrams/liter)</u>	<u>N-NO Produced (milligrams/liter)</u>
OH	~ 200	1.44
OH	~ 200	2.44
H ₂ O _p	~ 160	40
H ₂ O	~ 200	65
H ₂ O _{ap}	~ 200	48

References

6. C. H. Bamford, "A Study of the Photolysis of Organic Nitrogen Compounds, Part I Dimethyl - and Diethyl-Nitrosamines, Part II Aliphatic Amines," Chemical Society Journal, 12 (1939), p. 12.
7. H. Ballwag and D. Schmahl, "Über Photolyse bei Nitrosaminen," Naturwissen Shaften, 54 (5) (1967), p. 116.
8. D. Daiber and R. Preusemann, "Quantitative colorimetrische Bestimmung organischer N-Nitroso-Verbindung durch photochemische Spaltung der Nitrosaminbindung," Z. Anal. Chem., 206 (1964), p. 206.

The theoretical nitrogen content of a 200-milligram/liter NDMA solution is 65 milligrams/liter N. The acidified sample, H_2O_{ap} , may be low because the acidification may cause some of the NO_2 to be converted to NO and volatilized.

Comparison of the photolysis rate under different temperatures and light intensities during the day gave minimal differences. This probably occurs because the UV absorption of clouds is small.

Although data is not available, there is some evidence for the rate of photolysis being faster in the gas phase than in the aqueous phase. This means that if the NDMA is volatilized from the caustic solutions then it would probably be photochemically degraded. In order to evaluate this hypothesis, several simple gas phase photolysis experiments were conducted.

This study presented several problems. For unknown reasons, direct injection into the gas chromatograph of the gaseous NDMA caused the detector to become unstable, giving no quantitative results, and it became necessary to develop a new technique for analysis. Since NDMA absorbs strongly in the UV, this seemed a reasonable method to use.

A GC septum was glued to the top of the filling hole of a regular 5-centimeter liquid spectrophotometer cell providing a gas tight seal. Benzene was injected into the cell and allowed to volatilize. The spectra were then recorded at various times over a 6-hour period verifying that the cell was not leaking.

A GC liquid syringe was used to withdraw a small amount of pure NDMA and the liquid was deposited on the floor of the cell. The NDMA was allowed to volatilize for several minutes and then the absorbance was measured at 230 nanometers on a Coleman 55 spectrophotometer. The gas cell was then taken outside and placed in the direct sunlight. After 15 minutes, the cell was brought inside and the absorbance measured. If the absorbance figure could be quantitated from the standard curve of aqueous NDMA concentration versus absorbance, this value was used as the initial value and the cell was replaced in the sun. If the absorbance figure was too high to be quantitated, the sample was returned to the sun and the procedure repeated until a quantifiable value was obtained.

Once an initial reading was obtained, the sample was placed in the sun and at various times the absorbance was measured. The data obtained in this manner is plotted in Figure 6. The curves resemble those of the liquid studies with the average half-life of the NDMA in the gas phase being approximately 80 minutes. This is significantly shorter than the aqueous phase photolysis which has a half-life of 2.5 hours (Figure 3).

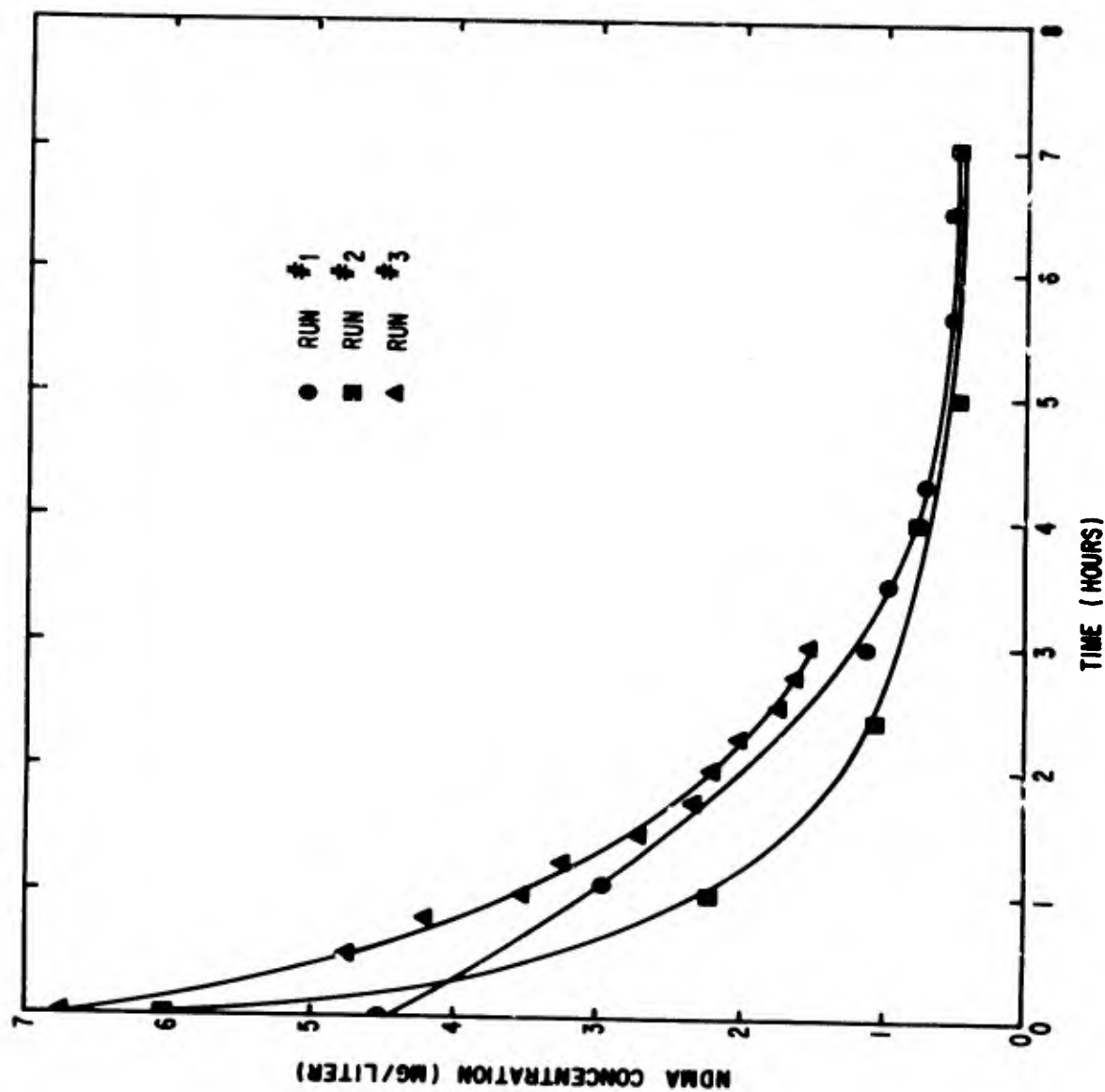


Figure 6. The Concentration of Gas Phase NDMA as a Function of Time

SECTION V

CONCLUSIONS

From the previous discussion, the following conclusions can be summarized:

1. NDMA is easily evaporated and photolyzed in aqueous solutions.
2. The rate of evaporation is greater at higher pHs; however, the rate of photolysis is greater in acid solutions.
3. Nitrite severely inhibits the photolysis of NDMA in acid and neutral pHs.
4. An increase in ionic strength slightly increases the evaporation rate.
5. The gas phase photolysis rate is approximately twice that found for the aqueous phase photolysis.

The implications of the above results for lagooning of the caustic NDMA waste stream are that the majority of the NDMA will volatilize from the solutions very rapidly unless the caustic is neutralized. If the waste is neutralized (assuming the resulting heat of neutralization does not distill off the NDMA), then photolysis would predominate unless nitrite is present, in which case, little of the NDMA would leave the lagoon either by volatilization or photolysis.

REFERENCES

1. N. Sen, et al, "Diethylnitrosamine and Other N-Nitrosamines in Foods," Analytical Chemistry, 52 (1969), p. 47.
2. A. Ayanaba, W. Verstraete, and M. Alexander, "Formation of Dimethylnitrosamine, A Carcinogen and Mutagen, in Soils Treated with Nitrogen Compounds," Soil Science Society of America, Proceedings, 37 (1973), p. 565.
3. A. Ayanaba, W. Verstraete, and M. Alexander, "Possible Microbial Contributions to Nitrosamine Formation in Sewage and Soil," National Cancer Institute Journal, 50 (1973), p. 811.
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5. A. L. Fridman, F. M. Mukhametshin, and S. S. Novikov, "Advances in the Chemistry of Aliphatic N-Nitrosamines," Russian Chemical Reviews, 40 (1) (1974), p. 34.
6. C. H. Bamford, "A Study of the Photolysis of Organic Nitrogen Compounds, Part I Dimethyl - and Diethyl-Nitrosamines, Part II Aliphatic Amines," Chemical Society Journal, 12 (1939), p. 12.
7. H. Ballwag and D. Schmahl, "Über Photolyse bei Nitrosaminen," Naturwissen Schaffen, 54 (5) (1967), p. 116.
8. D. Daiber and R. Preusemann, "Quantitative colorimetrische Bestimmung organischer N-Nitroso-Verbindung durch photochemische Spaltung der Nitrosaminbindung," Z. Anal. Chem., 206 (1964), p. 206.

LIST OF SYMBOLS

H_2O	water solution
OH	20 percent caustic solution
H_2O_n	nitrite added (1 gram)
H_2O_p	covered with a pyrex plate (photolysis only)
H_2O_s	shaded
H_2O_a	acid added to pH 3.5
H_2O_{Cl}	sodium chloride added (1 gram)
H_2O_B	25 ml beaker
H_2O_{as}	acidified and shaded
OH _s	25 percent caustic and shaded
H_2O_{ap}	acidified and covered with pyrex plate
OH _p	25 percent caustic and covered with pyrex plate
H_2O_{an}	acidified with nitrite added
H_2O_{ps}	covered with pyrex plate and shaded
OH _n	25 percent caustic with nitrite added
H_2O_{pn}	covered with pyrex plate with nitrite added
OH _{pn}	25 percent caustic pyrex covered with nitrite added